(11) Publication number:

0 160 996

A₂

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 85105700.0

(22) Date of filing: 09.05.85

(51) Int. Cl.4: **G** 03 **C** 5/54

G 03 C 1/02, G 03 C 1/42 C 07 C 147/06

(30) Priority: 09.05.84 JP 92558/84

(43) Date of publication of application: 13.11.85 Bulletin 85/46

(84) Designated Contracting States: DE GB NL

(1) Applicant: FUJI PHOTO FILM CO., LTD. 210 Nakanuma Minami Ashigara-shi Kanagawa 250-01(JP)

(72) Inventor: Yabuki, Yoshiharu c/o Fuji Photo Film Co., Ltd. No. 210, Nakanuma Minami Ashigara-shi Kanagawa(JP)

(72) Inventor: Kawata, Ken c/o Fuji Photo Film Co., Ltd. No. 210, Nakanuma Minami Ashigara-shi Kanagawa(JP)

[72] Inventor: Hirai, Hiroyuki c/oFuji Photo Film Co., Ltd. No. 210, Nakanuma Minami Ashigara-shi Kanagawa(JP)

(74) Representative: Patentanwälte Grünecker, Dr. Kinkeldey, Dr. Stockmair, Dr. Schumann, Jakob, Dr. Bezold, Meister, Hilgers, Dr. Meyer-Plath Maximilianstrasse 58 D-8000 München 22(DE)

64 Heat developable light-sensitive material.

(57) A heat developable light-sensitive material capable of giving images of high density and less fog in a short period of time, and which is excellent in stability. The heat developable light-sensitive material comprises a support and is formed thereon a heat developable light-sensitive layer, wherein said light-sensitive material contains at least one compound selected from the group consisting of compounds represented by formula (I) or (II) as a base precursor:

diacidic base; M represents an alkali metal or an alkaline earth metal; and m represents 1 when B represents monoacidic base and represents 2 when B represents diacidic base, and m' represents the valence number of M.

wherein R represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group or a heterocyclic group; X represents a substituent; P represents an integer of 0 to 4; B represents a monoacidic base or

HEAT DEVELOPABLE LIGHT-SENSITIVE MATERIAL

FIELD OF THE INVENTION

This invention relates to a heat developable lightsensitive material containing a base precursor.

BACKGROUND OF THE INVENTION

A heat developable light-sensitive material usually contains a base or a base precursor in the light-sensitive material for accelerating the development by heating. Also, in this case, it is preferred to use a base precursor capable of releasing a basic material by heat decomposition from the view point of the shelf life of the light-sensitive material.

Typical examples of the base precursor are described in U.K. Patent No. 998,949. Preferred base precursors are salts of carboxylic acids and organic bases. Useful carboxylic acid includes trichloroacetic acid, trifluoroacetic acid, etc., and useful organic base includes guanidine, piperidine, morpholine, p-toluidine, 2-picoline, etc. Guanidine trichloroacetate described in U.S. Patent No. 3,220,846 is particularly useful for such a purpose. Also, the aldonamides described in Japanese Patent Application (OPI) No. 22,625/'75 are decomposed at high temperature to form a base and are preferably used.(the term "OPI" indicates an unexamined published patent application open to public inspection).

However, many of these base precursors require
a relatively long period of time for obtaining images
and cause severe fog. Also, these base precursors
have the disadvantages that they are easily influenced
by air and humidity, to decompose and to change photographic characteristics of the light-sensitive material,
or greatly reduce the shelf life of the lightsensitive materials containing them.

For overcoming such a disadvantage, sulfonyl
acetates are proposed in Japanese Patent Application

(OPI) No. 168,441/'84. These materials are excellent

from the view point of providing images having a high

density in a short period of time, but are still not

totally sufficient in providing high density, or cause

a side action of forming severe fog. Furthermore, some

of the above-described base precursors are insufficient

with respect to the shelf life of the light-sensitive

material before heat development.

SUMMARY OF THE INVENTION

An object of this invention is to provide a heat developable light-sensitive material capable of giving images of high density in a short period of time without being accompanied by the aforesaid disadvantages.

Another object of this invention is to provide a heat developable light-sensitive material containing a

novel base precursor capable of giving images having high density and less fog.

Still another object of this invention is to provide a heat developable light-sensitive material excellent in stability with the passage of time.

The terminology "stability with the passage of time" refers to the time during storage of a heat developable light-sensitive material before heat development, the heat developable light-sensitive

10 material shows less change of photographic performance such as the maximum density, the minimum density, the sensitivity, etc.

It has now been discovered that the above-described objects of this invention can be attained by the heat

15 developable light-sensitive material containing at least one of compounds represented by formula (I) or (II)

$$R-SO_2 \xrightarrow{SO_2CH_2COOH \cdot B_1/m} X_p$$
 (I)

$$R-SO_2 \xrightarrow{SO_2CH_2COOM_1/m'} X_p$$
 (II)

wherein R represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, an substituted or unsubstituted alkynyl group, a substituted or

unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a heterocyclic ring but does not represent a carboxymethyl group; X represents a substituent; p represents an integer of 0 to 4; B represents a mono- or di-acidic base; M represents an alkali metal or an alkaline earth metal, m represents 1 when B represents monoacidic base and represents 2 when B represents diacidic base and m' represents the valence number of M.

DESCRIPTION OF PREFERRED EMBODIMENTS

10

In formulae (I) and (II), the alkyl group, cycloalkyl group, alkenyl group, and alkynyl group represented by R preferably have from 1 to 8 carbon atoms, and the aralkyl group and aryl group represented 15 by R preferably have at most 8 carbon atoms. It is preferred that the heterocyclic ring shown by R has at least one of nitrogen atom, an oxygen atom and a sulfur atom as a hetero atom of a 5- or 6-membered heterocyclic ring. Each group represented by R may be 20 substituted and preferred examples of the substituent are an alkyl group, an alkyl or aryl sulfonyl group, a sulfamoyl group, an N-alkyl- or N-arylsulfamoyl group, a carbamoyl group, an N-alkyl or an arylcarbamoyl group, an alkyl or arylsulfonamido group, an alkyl or arylacylamino group, a halogen atom, and a hydroxycarbonyl 25

group, etc. These substituents may further hav**0160996** stituent selected from groups disclosed hereinafter as preferred examples of X.

Specific examples of the groups shown by R are a methyl group, an ethyl group, a butyl group, an octyl group, a 2-ethylhexyl group, a phenyl group, a p-chlorophenyl group, a p-bromophenyl group, a p-methyl-phenyl group, a m-(diethylsulfamoyl)phenyl group, a l-naphthyl group, a 2-naphthyl group, a benzyl group, a pyridyl group, a pyrazolyl group, imidazolyl group, etc.

5

10

15

20

25

It is desirable that B is a base which is conventionally used in a heat developable light-sensitive material, that is, a mono- or di-acidic base having pKa of 7 or higher and having not more than 12 carbon atoms, and B is preferably a low volatile base havig pKa of 10 or higher and a boiling point of 150°C. or higher. More preferably, B represents organic bases, especially, a monoacidic or diacidic nitrogen-containing sulfer-free base, for example, aromatic or aliphatic amines or diamines, piperidines piperadines, guanidines, cyclic guanidines, amidines, cyclic amidines, tetraalkylammonium hydroxides, etc. Preferred examples of B are dimethylamine, diethylamine, piperidine, piperadine, ethylenediamine, N,N-dimethylethylenediamine, acetamidine, diazabicylononene. diazabicycloundecene, tetramethylammonium hydroxide, tetraethylammonium hydroxide, $\langle NH_2, H \rangle$ $N \rightarrow CH_3$, $N \rightarrow NH_2$ $H_2N \rightarrow C=NH$,

$$CH_3NH$$
 $C=NH$, CH_3NH
 $C=NH$, CH_3NH
 $C=NH$, CH_3
 $C=NH$, CH_3

tetramethylenediamine, N,N,N'N'-tetramethyltetramethylenediamine, etc.

X preferably does not include a carboxymethyl-5 sulfonyl group. Preferred examples of X are a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an alkoxy group, an aryloxy group, an aryl group, an acylamino group, an acyl group, a cyano group, an alkylsulfonylamino group, a nitro 10 group, an arylsulfonylamino group, an alkylsulfonyl group, an arylsulfonyl group, a sulfamoyl group, a substituted sulfamoyl group, a carbamoyl group, a substituted carbamoyl group, an alkylthio group, an arylthio group, an alkoxycarbonyl group, an aryloxycarbonyl 15 group, an alkyl or aryl acyloxy group, $-OM_{1/m}$, $-COOM_{1/m}$, -OH·B $_{1/m}$ (wherein -OH is phenolic), -COOH·B $_{1/m}$, wherein M, B, m and m' have same definitions as defined hereinabove. In these groups, an alkyl group and an aryl group may be further substituted.

Preferred examples of M are Na+, K+, Cs+, Ba++, etc.

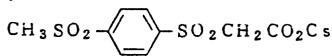
It is preferred that the carboxymethylsulfonyl group be at a para-position to the position of the sulfonyl group (RSO₂-).

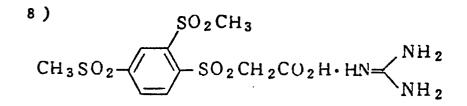
Specific examples of the basic precursor are illustrated below but the invention is not limited to these materials.

CH₃SO₂
$$\longrightarrow$$
 SO₂CH₂CO₂H·HN $\stackrel{\text{NH}_2}{\sim}$ NH₂

CH₃SO₂—
$$SO_2$$
CH₂CO₂H·HN= $N(CH_3)_2$

(
$$CH_3SO_2$$
 — $SO_2CH_2CO_2$)₂ Ba





9)
$$C\ell$$

$$CH_3SO_2 \longrightarrow SO_2 CH_2 CO_2 H \cdot HN \longrightarrow NH_2$$

$$NH_2$$

10)
$$C_4 H_9 SO_2 \longrightarrow SO_2 CH_2 CO_2 H \cdot HN \longrightarrow NH_2$$

$$NH_2$$

11)
$$C_8H_{17}SO_2 \longrightarrow SO_2CH_2CO_2H \cdot HN \longrightarrow NH_2$$

$$NH_2$$

1 2)
$$C_2H_5 \longrightarrow CHCH_2SO_2 \longrightarrow SO_2CH_2CO_2H \cdot HN \longrightarrow NH_2$$

$$C_4H_9 \longrightarrow CHCH_2SO_2 \longrightarrow SO_2CH_2CO_2H \cdot HN \longrightarrow NH_2$$

0160996

14)

$$CH_3SO_2$$

$$SO_2CH_2CO_2H \cdot HN = NHCH_3$$

$$NH_2$$

15)

16)

17)

$$\sim$$
 SO₂- \sim SO₂CH₂CO₂ K

0160996

20)

21)

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

22)

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$$

Br
$$\sim$$
 SO₂ \sim NH \sim

24)

$$CH_3$$
 \longrightarrow SO_2 CH_2 CO_2 $H \cdot NH =$ NH_2 NH_2

25)

26)

$$CH_3$$
 CH_2
 CH_3
 CH_2
 $CH_2CO_2H \cdot NH_2$
 NH_2

27)

$$\left(\left(\sum_{SO_2 \leftarrow SO_2 \leftarrow CH_2 \leftarrow CO_2} \right)_2 \quad \text{B a}$$

$$SO_2$$
 SO_2 CH_2 CO_2 K

$$\begin{array}{c} 29) \\ \text{HO}_2\text{C} \longrightarrow \text{SO}_2 \longrightarrow \text{SO}_2\text{CH}_2\text{CO}_2\text{H} \cdot 2\text{NH} \Longrightarrow \begin{pmatrix} \text{NH}_2 \\ \text{NH}_2 \end{pmatrix} \\ \text{30)} \\ \longrightarrow \text{SO}_2 \longrightarrow \text{SO}_2\text{CH}_2\text{CO}_2\text{H} \cdot \text{NH} \Longrightarrow \begin{pmatrix} \text{NH}_2 \\ \text{NH}_2 \end{pmatrix} \\ \text{(C}_2\text{H}_5)_2\text{NSO}_2 \\ \end{array}$$

The base precursors of this invention can be prepared by the following synthesis methods.

- a) An arylsulfone having an appropriate releasable group (e.g., halogen) is reacted with thioglycolic acid in the presence of a base to form a sulfide and then the sulfide is oxidized to form α-sulfonylacetic acid. The salt forming method is conventional.
- b) An arylsulfone is reacted with chlorosulfonic acid and the reaction product is reduced with sodium 10 sulfite to form sulfinic acid, which is condensed with an α-haloacetic acid ester to form an α-sulfonyl acetic acid ester. Then, by alkali-hydrolyzing the product at room temperature, α-sulfonylacetic acid is obtained. The salt formation is performed by a conventional method.
- Then, practical synthesis examples are shown below.

Synthesis Example 1

Synthesis of Base Precursor (1):

To 600 ml of chlorobenzene were added 272 g of anhydrous aluminum chloride and 229 g of methanesulfonyl chloride and the mixture was heated on a steam bath for 6 hours with stirring. The solution thus formed was poured into ice-water, and then the produce was extracted with 400 ml of methylene chloride. Methylene chloride was distilled off from the extract under reduced pressure.

25 To the residue thus formed was added 300 ml of methanol,

the mixture was cooled to 15°C, and crystals thus deposited were collected by filtration to provide 212 g 1-chloro-4-methylsulfonyl benzene having a melting point of 92 to 94°C.

To 1.6 liters of dimethylformamide were added

144 g of thioglycolic acid (85% in purity) and 532 g of
a 28% methanol solution of sodium methoxide to form the
disodium salt of thioglycolic acid. To the salt was
added 200 g of 1-chloro-4-methylsulfonyl benzene pre
10 pared above and while distilling off methanol, the mixture
was heated to 100°C for 6 hours with stirring, whereby
a large amount of a white salt deposited. The reaction
mixture thus formed was added to an aqueous hydrochloric
acid solution and the product thus formed was extracted

15 twice, each time with 400 ml of methylene chloride.

Then, the methylene chloride was distilled off under reduced pressure, and to the residue thus formed were added 270 ml of toluene and 30 ml of ethyl acetate.

The reaction mixture was cooled to 5°C and p-methyl
sulfonylphenylsulfenylacetic acid thus deposited was collected by filtration. The amount of the product was 120 g and the metling point was 136 to 139°C.

To 600 ml of water were added 120 g of p-methyl-sulfonylphenylsulfenylacetic acid and 1 g of sodium

25 tungestinate, and then 120 g of 35% hydrogen peroxide was

added dropwise thereto at a temperature below 85°C. Furthermore, after stirring the mixture, the reaction mixture was cooled and crystals thus deposited were collected by filtration to provide 130 g of p-methyl-sulfonylphenylsulfonylacetic acid. The melting point thereof was 191 to 193°C (decompd.).

To a mixture of 27.8 g of p-methylsulfonylphenylsulfonylacetic acid and 140 ml of methanol was added
dropwise with care an aqueous solution of about 9 g of
guanidine carbonate to neutralize the compound. Crystals
thus formed were collected to provide 29.0 g of Base
Precursor (1). The melting point was 246 to
250°C (decompd.).

Synthesis Example 2

15 Synthesis of Base Precursor (23):

From 200 g of anhydrous aluminum chloride, 153 ml of benzenesulfonyl chloride, 138 ml of bromobenzene, and 600 ml of methylene chloride was prepared 220 g of p-bromophenyl-phenyl-sulfone according to the method of

20 Journal of Chem. Soc., p 2508 (1960). To 100 ml of chlorosulfonic acid was added 100 g of p-bromophenyl-phenylsulfone, and after stirring the mixture for 4 hours at 130 to 140°C, the mixture was poured into ice water to provide 121 g of 3-(4-bromophenylsulfonyl)benzene
25 sulfonyl chloride.

To 150 ml of water was added 85 g of sodium sulfite and then 54 g of 3-(4-bromophenylsulfonyl)benzenesulfonyl chloride was added thereto. After stirring the mixture for 2 hours at 50°C, the reaction mixture thus obtained was ice-cooled and crystals thus formed were collected 5 by filtration. To the crystals thus obtained were added 40 ml of water, 40 ml of acetonitrile and 15 ml of methyl chloroacetate followed by refluxing for 2 hours. The reaction mixture thus formed was extracted with chloroform and then chloroform was distilled off from 10 the extract to provide 32.7 g of oily 3-(4-bromophenylsulfonyl)phenylsulfonylacetic acid methyl ester. Then, the oily product thus obtained was added to a mixture of 60 ml of water, 60 ml of methanol, and 8.1 g of potassium hydroxide and the resultant mixture was stirred 15 for one hour at room temperature. After adding 20 ml of 35% hydrochloric acid to the reaction mixture, the mixture was ice-cooled and crystals thus deposited were collected by filtration to provide 25.4 g of 3-(4bromophenylsulfonyl)phenylsulfonylacetic acid. By 20 neutralizing 21 g of the crystals thus obtained with 4.5 g of guanidine carbonate as in Synthesis Example 1, 22.3 g of Base Precursor (23) was obtained. The melting point was 85°C and the decomposition point was 95°C.

Other base precursors could be also prepared in an

analogous manner as above, and the melting points of typical precursors are shown in the following table.

Melting Point

Basic Precursor

	(1)		246-250°C(decomd.)
5	(2)		232-236°C(decomd.)
	(6)		above 250°C
	(8)		190°C(decomd.)
	(9)		106°C(decomd.)
	(11)		172-175°C(decomd.)
10	(12)		91°C(decomd.)
	(13)		above 250°C
	(15)		137-139°C(decomd.)
	(16)		132-133°C(decomd.)
	(20)		above 250°C
15	. (21)		152-153°C(decomd.)
	(22)		147-149°C(decomd.)
	(23)		85°C(decomd. at 95°C)
	(24)		168-170°C(decomd.)
	(26)		175-178°C
20	(29)		85-90°C(decomd.)
	(30)		125-128°C(decomd. at 170°C)
	(31)		175-180°C
	In the present	invention	a heat developable silver
	In the bresent	THACHETOH	a more actorohance actives

halide light-sensitive material may be used as a heat

developable light-sensitive material. The silver halide light-sensitive material comprises a support having coated thereon at least one silver halide emulsion layer comprising a silver halide dispersed in a binder. The silver halide light-sensitive material may further have at least one of an interlayer, a filter layer, an antihalation layer, a protective layer, and an image fixing (receiving) layer.

The base precursor of the present invention may be
incorporated into any of these layers; however, it is
preferably incorporated in a silver halide emulsion layer.
When the fixing layer is provided on a different support
from that on which the silver halide emulsion layer is
coated, the base precursor may be incorporated to this
fixing layer. In this case a fixing material having a
fixing layer and a heat developable light-sensitive material are used in combination.

Examples of silver halide include silver chloride, silver chlorobromide, silver chloroiodide, silver bromide, 20 silver iodobromide, silver chloroiodobromide, silver iodide. An organic silver salt such as silver benzotriazole may also be incorporated to a silver halide emulsion as an oxidizing agent.

The base precursor is incorporated into at least one of above-described layers by dissolving it into water or

an organic solvent having a low boiling point (such as methanol) or a high boiling point (such as those disclosed hereinafter as a solvent for a dye providing material), and dissolving or dispersing the thus obtained solution to a coating composition for the layer. The base precursor may also be dispersed in a binder solution directly.

The effect of the base precursor of this invention is particularly remarkable when used together with a light-sensitive silver halide emulsion that has been spectrally sensitized. That is, when the precursor is used together with a spectrally sensitized light-sensitive silver halide emulsion, the extent of increasing the image density is particularly high.

The spectral sensitization of silver halide emulsions is performed using methine dyes, etc. Examples of dyes useful for spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxonole dyes. Particularly useful dyes are cyanine dyes, merocyanine dyes, and complex merocyanine dyes. For these dyes, nuclei usually utilized for cyanine

For example, there are pyrroline nuclei, oxazoline nuclei,

dyes can be applied as basic heterocyclic ring nuclei.

25 thiazoline nuclei, pyrrole nuclei, oxazole nuclei,

thiazole nuclei, selenazole nuclei, imidazole nuclei, tetrazole nuclei, pyridine nuclei, etc.; the nuclei formed by the fusion of aliphatic hydrocarbon rings to the foregoing nuclei and the nuclei formed by the fusion of aromatic hydrocarbon rings to the foregoing nuclei, such as indolenine nuclei, benzindolenine nuclei, indole nuclei, benzoxazole nuclei, naphthoxazole nuclei, benzo-thiazole nuclei, naphthothiazole nuclei, benzoselenazole nuclei, benzimidazole nuclei, quinoline nuclei, etc.

10 These nuclei may be substituted on carbon atoms.

20

For the merocyanine dye or complex merocyanide dye can be applied a 5- or 6-membered heterocyclic nucleus such as a pyrazolin-5-one nucleus, thiohydantoin nucleus, a 2-thiooxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus, a thiobarbituric acid nucleus, etc., as a nucleus having a ketomethylene structure.

These sensitizing dyes may be used individually or as a combination thereof. A combination of sensitizing dyes is frequently used for supersensitization.

Examples of useful sensitizing dyes are described in, for example, German Patent No. 929,080; U.S. Patent Nos. 2,493,748; 2,503,776; 2,519,001; 2,912,329; 3,656,959; 3,672,897; 3,694,217; 4,025,349; 4,046,572; U.K. Patent No. 1,242,588; Japanese Patent Publication

Nos. 14,030/69 and 24,844/77.

The amount of the sensitizing dye is from 0.001 g to 20 g, and preferably from 0.01 g to 2 g per 100 g of silver of the silver halide emulsion.

The base or the base precursor of this invention can be used in an amount of a wide range. The useful range is not more than 50% by weight, usually not less than 0.001% by weight, preferably 0.01% by weight to 40% by weight of the total weight of the dry coated layer of a light-sensitive material.

In this invention, silver may be used as the imageforming material or various image-forming materials may be used in various manners.

For example, couplers which form color images by

15 combining with the oxidation product of a developing
agent which is conventionally used for liquid development
can be used as the image-forming materials in this invention. This includes 5-pyrazolone couplers, pyrazolobenzimidazole couplers, cyanoacetylcumarone couplers,

20 open chain acylacetonitrile couplers, etc., as magenta
couplers; acylacetamido couplers (e.g., benzoylacetanilides,
pyvaloylacetanilides, etc.), etc. as yellow couplers; and
naphthol couplers, phenol couplers, etc., as cyan
couplers. Non-diffusible couplers having a hydrophobic

25 group, a so-called ballast group, in the molecule, or

polymerized couplers are preferred. The couplers may be four equivalent or two equivalent to silver. Also, the couplers may be colored couplers having a color correction effect or so-called DIR couplers capable of releasing a development inhibitor with the progress of development.

Also, dyes forming positive color images by a photographic silver dye bleaching process, for example, the dyes described in <u>Research Disclosure</u>, April 1976, pages 30-32 (RD-14433), <u>ibid</u>., December 1976, pages 14-15 (RD-15227), U.S. Patent 4,235,957 and the leuco dyes described in U.S. Patents 3,985,565; 4,022,617, etc.

Also, the dyes having introduced therein a nitrogen-containing heterocyclic ring group described in <u>Research</u>
Disclosure, May 1978, pages 54-58, (RD-16966) can be used.

15

Furthermore, a dye-providing materials releasing a mobile dye by utilizing a coupling reaction with a reducing agent oxidized by an oxidation reduction reaction with silver halide or an organic silver salt upon heat development at high temperature described in European Patent Application (published) Nos. 79,056 and 67,455; West German Patent No. 3,217,853, etc., and a dye-providing materials releasing a mobile dye as the result of an oxidation-reduction reaction with silver halide or an organic silver salt upon heat development at a high

temperature described in European Patent Application (published) Nos. 76,492, 66,282, 120,306 and 119,470; West German Patent No. 3,215,485, can be used.

The dye-providing materials used in this invention are preferably shown by following formula (CI)

$$(Dye-X)_{q}-Y$$
 (CI)

wherein Dye represents a dye moiety which becomes a mobile dye when released from the molecule and has, preferably, a hydrophilic group. As such dyes, there are an azo dye, an azomethine dye, an anthraquinone dye, a naphthoquinone dye, a styryl dye, a nitro dye, a quinoline dye, a carbonyl dye, a phthalocyanine dye, etc., and specific examples of them are shown below. In addition, these dyes can be used as the form of having their absorption temporarily shifted to a short wavelength side, which can recover the original color by development.

For example, the dyes described in European Patent Application (published) No. 76,492 can be thus utilized.

X in the aforesaid formula represents a simple bond or a linkage group, such as, for example, -NR- group (wherein R represents a hydrogen atom, an alkyl group or a substituted alkyl group), -SO₂- group, -CO- group, an alkylene group, a substituted alkylene group, a phenylene group, a substituted phenylene group, a naphthylene group, 25 a substituted naphthylene group, -O- group, -SO- group,

or a group formed by the combination of two or more above-described groups.

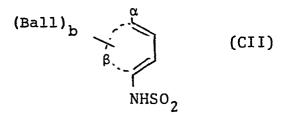
Y in the above formula represents a group having a property of releasing Dye in direct or inverse proportion to a light-sensitive silver salt having imagewise latent images to form a difference in diffusibility between the released dye and the compound shown by Dye-X-Y.

The group represented by Y is now explained in 10 detail.

15

Y in formula (CI) described above is selected so that the compound represented by formula (CI) becomes a non-diffusible image-forming compound which is oxidized and self-cleaved as result of development to provide a diffusible dye.

An example of Y effective for this type of compound is an N-substituted sulfamoyl group. An example of Y is a group represented by formula (CII)



20 wherein, β represents a nonmetallic atomic group necessary for forming a benzene ring, said benzene ring may be condensed with a carbon ring or a heterocyclic ring

to form, for example, a naphthalene ring, a quinoline ring, a 5,6,7,8-tetrahydronaphthalene ring, a chroman ring, etc.

 α in formula (CII) represents a group represented $-0G^{11}$ or $-NHG^{12}$ (wherein G^{11} represents a hydrogen atom or a group forming a hydroxy group by hydrolysis and G^{12} represents a hydrogen atom, an alkyl group having from 1 to 22 carbon atoms, or a hydrolyzable group, and Ball represents a ballast group.

Practical examples of Y are described in Japanese Patent Application (OPI) Nos. 33,826/'73 and 50,736/'78.

10

Another example of Y suitable for the compound of this type is the group represented by formula (CIII)

(Ball)
$$b$$
 NH-SO₂ (CIII)

wherein Ball, α, and b have the same meaning as in the case of formula (CII) and β' represents an atomic group necessary for forming a carbocyclic ring, such as a benzene ring, and said benzene ring may be condensed with a carbon ring or a heterocyclic ring to form a naphthalene ring, a quinoline ring, a 5,6,7,8-tetrahydronaphthalene ring, a chroman ring, etc. Practical examples of Y of this type are described in Japanese Patent Application (OPI) Nos. 113,624/'76; 12,642/'81;

16,130/'81; 16,131/'81; 4043/'82; 650/'82 and U.S. Patent 4,053,312.

5

Furthermore, still other example of Y suitable for the compound of this type is the group represented by formula (CIV)

$$(Ball)_{b}$$

$$\beta''$$

$$\beta''$$

$$(CIV)$$

wherein Ball, α, and b have the same meaning as in the case of formula (CII) and β" represents an atomic group forming a heterocyclic ring such as a pyrozole ring, a pyridine ring, etc., said heterocyclic ring may be condensed with a carbon ring or a heterocyclic ring. Practical examples of Y of this type are described in Japanese Patent Application (OPI) No. 104,343/'76.

Furthermore, other example of Y suitable for the

15 compound of this type is the group represented by formula (CV)

$$\delta = 1000 \text{ (CV)}$$

wherein γ preferably represents a hydrogen atom, an substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted 20 heterocyclic ring group, or -CO-G²¹ (wherein G²¹ represents

 G^{23} -OG²², -S-G²², or -N G^{24} ; wherein G^{22} represents a hydrogen atom, an alkyl group, a cycloalkyl group, or an aryl group; G^{23} represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group, or an acyl group induced from an aliphatic carboxylic acid, an aromatic carboxylic acid or sulfonic acid; and G^{24} represents a hydrogen atom or an unsubstituted or substituted alkyl group); and G^{24} represents a condensed benzene ring.

Practical examples of Y of this kind are described in Japanese Patent Application (OPI) Nos. 104,343/'76; 46,730/'78; 130,122/'79; 85,055/'82, etc.

Moreover, as Y suitable for the compound of this type, there is the group represented by formula (CVI)

Ball
$$C=\epsilon$$
 (CVI)

$$C = \epsilon$$

$$C$$

wherein Ball is same as the case of formula (CII); ε represents an oxygen atom or =NG³² group (wherein G³² represents a hydroxy group or an amino group which may have a substituent); in this case, examples of the compound H₂N-G³² from which the =NG³² group is derived include hydroxylamine, hydrazines, semicarbazides,

thiosemicarbazides, etc.; β '" represents an atomic group forming a 5-membered, 6-membered or 7-membered saturated or unsaturated non-aromatic hydrocarbon ring; and G^{31} represents a hydrogen atom or a halogen atom such as fluorine, chlorine, bromine, etc. Practical examples of Y of this kind are described in Japanese Patent Application (OPI) Nos. 3819/'78; 48,534/'79, etc.

Examples of Y of the compound of this type include groups as described, for example, in Japanese Patent Publication Nos. 32,129/'73 and 39,165/'73; Japanese Patent Application (OPI) No. 64,436/'74; U.S. Patent No. 3,443,934, etc.

10

As still another example of Y, there is the group represented by formula (CVII)

15 $\alpha - C \xrightarrow{\qquad \leftarrow} C - C)_{\overline{n-1}} \overset{*}{C} - NHSO_{2} - CVII)$ $(CVII)_{\overline{n-1}} \times Nu$

wherein a represents OR⁴¹ or NHR⁴² (wherein R⁴¹ represents a hydrogen atom or a hydrolyzable moiety and R⁴² represents a hydrogen atom or an alkyl group having from 1 to 50 carbon atoms); A⁴¹ represents an atomic group necessary for forming an aromatic ring; Ball represents an organic immobilizing group disposed on an aromatic ring; m represents an integer of 1 or 2; when m is 2,

said Ball groups may be the same or different; X represents a divalent organic group having from 1 to 8 carbon atoms and forms a 5- to 12-membered ring with a nucleophilic group (Nu) and an electrophilic center (the carbon atom with *) formed by oxidation; Nu represents a nucleophilic group; n represents an integer of 1 or 2; and α is the same as in the case of above formula (CII). Practical examples of Y of this kind are described in Japanese Patent Application (OPI)

Furthermore, as other type of the compound shown by formula (CI), there is a nondiffusible image-forming compound which causes self ring closure in the presence of a base to release a diffusible dye, but substantially does not release the dye when the compound reacts with the oxidation product of a developing agent.

Examples of Y effective as a compound of this type include groups represented by formula (CVIII)

$$G^{55}$$
 G^{652}
 G^{51}
 G^{651}
 G^{652}
 G^{653}
 G^{654}
 G^{657}
 G^{657}
 G^{657}
 G^{657}

20 wherein α' represents an oxidizable nucleophilic group such as a hydroxy group, a primary or secondary amino group, a hydroxyamino group, a sulfonamido group, etc.,

or a precursor thereof; a" represents a dialkylamino group or an optional group defined in regard to a'; G⁵¹ represents an alkylene group having from 1 to 3 carbon atoms, a represents 0 or 1, G⁵² represents a substituted or unsubstituted alkyl group having from 1 5 to 40 carbon atoms or a substituted or unsubstituted aryl group having from 6 to 40 carbon atoms, G⁵³ represents an electrophilic group such as -CO-, -CS-, etc.; and ${\tt G}^{54}$ represents an oxygen atom, a sulfur atom, a selenium atom, a nitrogen atom, etc., and when G^{54} is a nitrogen 10 atom, it may be substituted by a hydrogen atom, a substituted or unsubstituted alkyl group having from 1 to 10 carbon atoms, or an aromatic residue having 6 to 20 carbon atoms, G^{55} , G^{56} and G^{57} each represents a hydrogen atom, a halogen atom, a group containing a carbonyl 15 group (e.g., an amide group and -COOH), a sulfamoyl group a sulfonamide group, an alkyloxy group having from 1 to 40 carbon atoms or represents the same group as defined for G^{52} , G^{55} and G^{57} together may form a ring, or G^{56} may be 20

$$G^{52}$$
 - $(G^{51})_a$ - $N - G^{53} - G^{54}$ - ,

25

wherein at least one of G^{52} , G^{55} , G^{56} and G^{57} represents a ballast group. Examples of Y of the compound of this type include groups as described, for example, in Japanese Patent Application (OPI) No. 63,618/'76.

Examples of Y suitable for the compound of this type include groups represented by formulae (CIX) and (CX):

5

10

wherein Nu⁶¹ and Nu⁶² (which may be the same or different) each represents a nucleophilic group or a precursor thereof; Z⁶¹ represents a divalent atomic group which is electrically negative to the carbon atom to which R⁶⁴ and R^{65} are substituted; R^{61} , R^{62} , and R^{63} each represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, or an acylamino group; when said R⁶¹ and R⁶² are adjacently disposed on a ring, they may form a condensed ring with the remaining molecule, or said R⁶² and R⁶³ may form a condersed ring with the remaining 15 part of the molecule; R⁶⁴ and R⁶⁵ (which may be the same or different) each represents a hydrogen atom, a hydrocarbon group or a substituted hydrocarbon group; and a

sufficiently large ballast group, Ball exists at least on the substituent R⁶¹, R⁶², R⁶³, R⁶⁴, or R⁶⁵ for making immobile the aforesaid compound. Practical examples of Y of this kind are described in Japanese Patent Application (OPI) Nos. 69,033/'78 and 130,927/'79.

Also, another Y suitable for the compound of this type, is the group represented by formula (CXI)

wherein Ball and β' are same as defined in formula (C III); G⁷¹ represents an alkyl group or a substituted alkyl group. Practical examples of Y of this kind are described in Japanese Patent Application (OPI) Nos. 111,628/'74 and 4,819/'77.

Moreover, another example of the compound shown by

15 formula (CI) above is a non-diffusible image-forming
compound which does not release a dye by itself, but
releases a dye when the compound reacts with a reducing
agent. In this case, it is preferred to use a compound
mediating the redox reaction (a so-called electron donor)

together with the image-forming compound.

As an example of Y effective for the compound of this type, there is a group shown by formula (CXII)

Ball
$$C - C - N - C$$
 (CXII)

- wherein Ball and B' are same as defined in formula (CIII) and G⁷¹ represents an alkyl group or a substituted alkyl group. Practical examples of Y of this kind are described in Japanese Patent Application (OPI) Nos. 35,533/ '78 and 110,827/'78.
- As still other example of Y suitable for the compound of this type, there is the group shown by formula (CXIII)

$$G^{55}$$
 G^{6}
 G^{50}
 G^{6}
 G^{50}
 G^{50}

wherein α'_{ox} and α''_{ox} each represents a group giving α' or α'' by reduction and α' , α'' , G^{51} , G^{52} , G^{53} , G^{54} , G^{55} , G^{56} , G^{57} , and α'' are same as the case of formula (C VIII). Practical examples of Y of this kind are described in Japanese Patent Application (OPI) NO.110,827/'78

and U.S. Patents 4,356,249 and 4,358,525.

5

10

15

Other examples of Y suitable for the compound of this type include groups represented by formulae (CXIV A) and (CXIV B)

$$\begin{array}{c|c}
 & (N_{uox})^{1} R^{64} \\
 & C \\
 & C \\
 & R^{65} \\
 & R^{65}
\end{array}$$
(CXIV A)

$$\begin{array}{c|c}
 & (N_{uox})^{1} \\
 & R^{63} & (N_{uox})^{2} \\
 & R^{62} & R^{64} & (CXIV B) \\
 & R^{62} & R^{61} - R^{65}
\end{array}$$

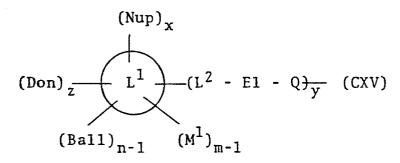
wherein $(N_{uox})^1$ and $(N_{uox})^2$, which may be the same or different, each represents an oxidized nucleopholic group and other symbols are the same as in the cases of formulae (CIX) and (CX). Practical examples of Y of this kind are described in Japanese Patent Application (OPI) Nos. 130,927/'79 and 164,342/'81.

In the patent specifications cited in regard to formulae (CXII), (CXIII), (CXIV A) and (CXIV B), electron donors which can be used with the aforesaid compounds are described.

Also, as other type of compound shown by general formula (I), there is further a linked donor acceptor

compound (LDA compound). This compound is a non-diffusible image-forming compound which causes a donor-acceptor reaction in the presence of a base to release a diffusible dye, but does not substantially release the dye when the compound reacts with the oxidation product of a developing agent.

Example of Y effective for the compound of this type, there is, for example, the group shown by following formula (CXV). Practical examples of Y of this kind are described in British Patent Application (published)
No. 2,140,927.



wherein n, x, y, and z are 1 or 2; m represents an integer of 1 or more; Don represents a group containing

15 an electron donor or a precursor moiety thereof; L¹

represents an organic group connecting Nup and -L²-E1-Q

or Don; Nup represents a precursor for a nucleophilic group; E1 represents an electrophilic center; Q represents a divalent group; Ball represents a ballast group; L²

20 represents a linkage group and M¹ represents an optional substituent.

The ballast group is an organic ballast group capable of rendering the dye image-forming compound nondiffusible, and it is preferred that the ballast group is a group containing a hydrophobic group having from 8 to 32 carbon atoms. Such an organic ballast group is bonded to the dye image-forming compound directly or through a linkage group (e.g., an imino bond, an ether bond, a thioether bond, a carbonamido bond, a sulfonamido bond, a ureido bond, an ester bond, an imido bond, a carbamoyl bond, a sulfamoyl bond, etc., either singly or as a combination thereof.

The dye-providing materials may be used solely or a combination of two or more. In the case of using a mixture, the same color may be formed by using two or more dyes, or black may be formed using two or more dyes.

Practical examples of the image-forming material for use in this invention are described in the patent specifications indicated above. Example compounds are shown below.

For example, the dye-providing materials shown by foregoing formula (CI) are as follows.

NC N-NH SO₂ NH OCH₂ CH₂OCH₃
OH
SO₂ NH
$$C_{4}H_{9}(t)$$

NC N-NH-OCH₂CH₂OCH₃
OH
SO₂NH
$$C_{4}H_{9}(t)$$
OC₁₆H₃3(n)

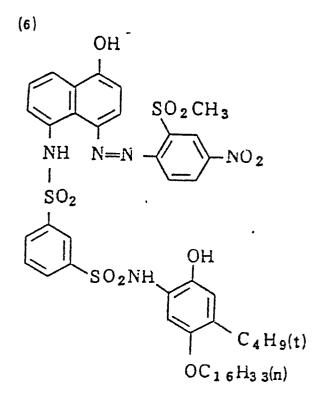
OH
$$SO_{2}N(C_{2}H_{5})_{2}$$

$$CH_{3}SO_{2}NH \qquad N=N \longrightarrow OCH_{2}CH_{2}OCH_{3}$$

$$OH$$

$$SO_{2}NH \qquad CH_{3}$$

$$C_{1}_{6}H_{3}_{3}O \qquad CH_{3}$$



(10)

(11)

OH
$$SO_{2}N(C_{2}H_{5})_{2}$$

$$CH_{3}SO_{2}NH \qquad N=N \longrightarrow OCH_{2}CH_{2}OCH_{3}$$

$$SO_{2}NH$$

$$(H_{3},C_{1},8)_{2}NOC \longrightarrow OH$$

OH
$$CON(C_{18}H_{37})_{2}$$

$$NHSO_{2}$$

$$SO_{2}NH$$

$$N=N$$

$$SO_{2}CH_{3}$$

$$SO_{2}N(C_{3}H_{7}-iso)_{2}$$

(14)

The above-described specific compounds are illustrated as non-limiting examples of the dye-providing materials for use in this invention.

5

10

15

25

In the present invention a dye-providing material which releases or produces a mobile dye corresponding to or reversely corresponding to a reduction reaction of a silver halide through a reducing agent may also be preferably used. Examples of such materials include coupler. a dye which is able to form positive color images by a photographic silver dye bleaching process, a dye having introduced therein a nitrogen-containing heterocyclic ring group, a dye-providing material which releases a mobile dye by a coupling reaction with a reducing agent which is oxidized by an oxidation reduction reaction with a silver halide or an organic silver salt upon heat development, a non-diffusible image-forming compound which causes self ring closure in the presence of a base to release a diffusible dye, but does not release the dye when the compound reacts with the oxidation product of a developing agnet, a non-20 diffusible image-forming compound which does not release a dye by itself but releases a dye when the compound reacts with a reducing agent, and a linked donor acceptor compound which is a nondiffusible image-forming compound and causes a donor-acceptor reaction in the presence of a base to release a diffusible dye, but does not substantially release the dye when the compound reacts with the oxidation product of a developing agent.

Many of the above-described materials fo and ano 996 imagewise distribution of a mobile dye by heat development corresponding to the exposed portion of a light-sensitive material, and a process for visualizing the dye image in a dye-fixing material (so-called diffusion transfer process) is described in the above-indicated patent specifications and European Patent Application (published) No. 119,615.

5

10

20

In the present invention, the dye providing material and other photographic additives may be introduced to the layer of the light sensitive material according on the method disclosed in column 13 of U.S. Patent 4,500,627.

In the present invention, developing agents and reducing agents as disclosed in column 49 of U.S. Patent 4,500,626 may be used.

In the present invention, silver halide and organic silver compounds as disclosed in columns 14-15 in U.S. Patent 4,500,627 may be used. Binders which are disclosed in column 15 of the same patent may also be used in the present invention.

When spectral sensitization is carried out in the

present invention sensitizing dyes disclosed in columns 15-16 of U.S. Patent 4,500,627 may be used in the manner according on the method disclosed therein.

Methods for exposure, development and after
treatment disclosed in column 20 of U.S. Patent

4,500,627 may be applied to the heat developable lightsensitive material of the present invention.

Supports, surfactants, hardening agents, mordants, dye transfer assistants, dye fixing layers, dye fixing 10 materials, etc., which are disclosed in U.S. Patent 4,500,627 may be used in the present invention.

Example 1

Preparation of Silver Iodobromide Emulsion

Gelatin (40 g) and KBr (26 g) were dissolved in water (3,000 ml). The solution was agitated at 50°C. A solution obtained by dissolving silver nitrate (34 g) in water (200 ml), and a solution (200 ml) obtained by dissolving dye I (0.02 g) shown hereinafter were added to the KBr solution over a period of 10 minutes. To this solution, a solution of KI (3.3 g) in water (100 ml) was added over a period of 2 minutes. The pH of the thus prepared silver idobromide emulsion was adjusted to precipitate the emulsion and the excess salt was then filtered out. The pH of the emulsion was adjusted to 6.0 to obtain a silver iodrobomide emulsion (yield: 400 g).

15 Preparation of Coupler Dispersion in Gelatin

2-dodecylcarbamoyl-l-naphthol (dye providing material (17) 5g), succinic acid-2-ethylhexyl ester sodium sulfonate (0.5 g) and tricresyl phosphate (TCP) (2.5 g) were dissolved in ethyl acetate (30 ml). The resulting solution was mixed with a 10 wt% gelatin solution (100 g) under agitation, and, the mixture was dispersed using a homogenizer for 10 minutes at 10,000 rpm.

A coating liquid having the composition indicated below was applied to a polyethylene terephthalate film base

to give a wet thickness of 60 μm and then dried to prepare a light-sensitive material.

(a)	Silver	iodobromide	emulsion	10	g
-----	--------	-------------	----------	----	---

(b) Coupler dispersion in gelatin 3.5 q

5 (c) Solution of base precursor (1) of the present invention 0.28 g

(d) Gelatin (10 wt% aq. sol.) 5

(e) Solution of 0.2 g of 2,6-dichloro-p-aminophenol dissolved in 17 ml of water

The light-sensitive material thus prepared was imagewise exposed using a tungsten lamp (2,000 lux) for 5 seconds. Then, the exposed material was heated uniformly on a heat block (150°C, 20 sec) to provide a negative dyan dye image. The image density was measured with a Macbeth transmission densitometer (Model TD-504): Dmin was 0.26 and Dmax was 2.13.

The above result indicates that the base precursor according to the present invention provides a high density. Dye ${\tt I}$

Example 2

In this example, a silver iodobromide emulsion of the same type as used in Example 1, and a dispersion of dye releasing material prepared as follows were used.

5 Preparation of Dispersion of Dye Releasing Material

of surfactant i.e. succinic acid-2-ethylhexyl ester sodium sulfonate and 5 g of tricresyl phosphate (TCP) were dissolved in 30 ml of ethyl acetate under heating at about 60°C. The resulting solution was mixed with a 10 wt% gelatin solution (100 g) under agitation, and the resulting mixture was dispersed using a homogenizer for 10 minutes at 10,000 rpm.

A light-sensitive composition was prepared from the following formulation.

- 15 (a) Light-sensitive silver iodobromide
 emulsion (as shown in Example 1) 25 q
 - (b) Dispersion of dye releasing material (2) 33 g
 - (c) 5 wt% Aqueous solution of
 the following compound: 10 ml

20

$$C_9H_{19}$$
 O CH_2CH_2O 10^{H}

(d) 10 wt% Aqueous solution of the following compound:

4 ml

25

(e) Base precursor (1) of the
 present invention

2.7 g

(f) Water

20 ml

The above components of (a) ∿ (f) were mixed and

5 dissolved under heating. The resulting solution was applied
onto a polyethylene terephthalate film base to give a wet
thickness of 30 µm and then dried to provide a light-sensitive
material. This material was imagewise exposed using a
tungsten lamp (2,000 lux) for 10 seconds and heated uniformly

10 on a heat block (150°C) for 20 seconds to provide sample A.

Sample B was prepared by following the same procedure as above except that 1.8 g of guanidinetrichloroacetic acid was used in place of the compound of this invention of (e) in Sample A, Sample C was prepared using 2.1 g of guanidine phenulsulfonylacetate in place of the aforesaid compound of this invention, and Sample D was prepared using 2.2 g of guanidine 3-sulfamoylphenylsulfonylacetate in place of the aforesaid compound of this invention and these samples were processed by the same manner as above.

20 Preparation of Image-receiving Material

Ten grams of methyl acrylate-N,N,N-trimethyl-N-vinyl-benzylammonium chloride copolymer (molar ratio of methyl acrylate to vinyl benzyl ammonium chloride is 1:1) was dissolved in water (200 ml), and the solution was mixed uniformly with 10 wt% lime-treated gelatin (100 g). The

resulting mixture was uniformly spread onto a paper base laminated with TiO, dispersed polyethylene, thereby forming an image-receiving layer of a uniform wet thickness of 90 µm. The layer was dried to provide an image-receiving material.

The image receiving material was dipped in water and recovered therefrom. Samples A, B, C and D of the lightsensitive material heated were superimposed on each sample of image-receiving material in such a manner that each of the light-sensitive layers was in contact with the image-receiving 10 layer, respectively.

After heating on a heat block (80°C) for 6 seconds, each image-receiving material was peeled from each lightsensitive material. A negative magenta image was formed on each image-receiving material. The density of each negative 15 image was measured with a Macbeth (RD-S19) reflection densitometer. The results were as follows.

	Sample No.			<u>le No</u> .	Dmax	<u>Dmin</u>
	A	(Present Invention)			1.95	0.15
	В	(Control)			2.14	0.58
20	С	(Ħ)	1.28	0.16
	D	(Ħ)	1.45	0.15

5

The above results show that the base precursor according to the present invention gives high maximum and low minimum densities.

Samples A, B, C and D were left to stand at 60°C for 2 days, and treated as above. The Dmin and Dmax of the image of Sample A were 0.23 and 2.01, Sample C were 0.20 and 1.33 and Sample D were 0.27 and 1.49 respectively, but fog occurred throughout the surface of sample B. Thus, the Sample of the present invention has an improved storage stability.

Example 3

The procedure of Example 2 was repeated except that

10 the base precursors shown in the following table were used.

The results are also shown in the same table.

	Sample No.	Base	Precursor	(g)	Dmax
	D	Compound	(2)	2.8	2.03
	E	Compound	(6)	2.5	1.79
15	F .	Compound	(9)	3.0	1.92
	G	Compound	(15)	3.2	2.00
	н	Compound	(16)	3.3	2.12
	I	Compound	(21)	2.3	1.83
	J	Compound	(23)	3.8	1.82
20	K	Compound	(25)	3.5	1.99

The above results show that base precursors according to the present invention give high maximum densities.

Example 4

In this example, an organic silver salt oxidizing 25 agent was used.

Preparation of Silver Benzotriazole Emulsion

Gelatin (28 g) and benzotriazole (13.2 g) were dissolved in water (3,000 ml). The resulting solution was agitated at 40°C. To this solution, a solution having silver nitrate (17 g) dissolved in water (100 ml) was added over a period of 2 minutes.

The resulting benzotriazole silver emulsion was pH-adjusted to precipitate, and the excess salt was filtered out. The emulsion was adjusted to a pH of 6.0, thereby providing a silver benzotriazole emulsion (yield: 400 g).

Using this silver benzotriazole emulsion, a light-sensitive coating composition was prepared from the following formulation.

(a) Silver iodobromide emulsion

15 (as prepared in Example 1) 20 g

- (b) Silver benzotriazole emulsion 10 g
- (c) Dispersion of dye releasing material(as prepared in Example 2)33 g
- (d) 5% Aqueous solution of the following

20 compound: 10 ml C_9H_{19} C_9H_{19} C_9H_{10}

(e) 10% Aqueous solution of the following

compound: H₂NSO₂N(CH₃)₂ 4 ml

(f) Base precursor (1) of the present invention 3 g

(g) Gelatin dispersion of the acid

precursor shown below 8 ml

5 (h) Water 12 ml

The gelatin dispersion of the acid presursor of the aforesaid component (g) was prepared as follows.

To 100 g of 1% aqueous solution of gelatin was added 10 g of the compound shown below and the compound was 10 pulverized for 10 minutes in a mill using 100 g of glass beads having a mean particle size of about 0.6 mm. By separating the glass beads by filtration, a gelatin dispersion of the acid precursor was obtained.

Above components (a) to (g) were mixed and by

20 following the same procedure as in Example 2 using the
mixture, Samples (A'), (B') and (C') were prepared.

The samples were also processed as in Example 2 and the
results thus obtained are shown below.

		<u>Sample</u>	_Dmax_	Dmin
	(A')	Containing Base Precursor (1) (This invention)	2.19	0.16
5	(B¹)	Containing Guanidine- trichloroacetic Acid (Comparison)	2.33	0.61
	(C¹)	Containing Guanidine Phenylsulfonylacetate (Comparison)	1.47	0.19

From the results, it can be seen that the sample of this invention containing the base precursor in this invention give both the high maximum density and the low minimum density.

Furthermore, after storing Samples (A'), (B') and (C') for 2 days at 60°C, and then processing in the same manner as above and the results showed that the minimum density and the maximum density were 0.23 and 2.21, respectively for Sample (A') and 0.20 and 1.52, respectively for Sample (C'), while Sample (B') was overall fogged. Thus, it can be seen that the sample of this invention show a good storage stability.

20 Example 5

Preparation of Silver Benzotriazole Emulsion Containing
Light-sensitive Silver Bromide

Benzotriazole (6.5 g) and gelatin (10 g) were dissolved in water (1,000 ml). The resulting solution was

agitated at 50°C. To this solution, a solution of silver nitrate (8.5 g) dissolved in water (100 ml) was added over a period of 2 minutes.

Then, a solution of potassium bromide (1.2 g)

5 dissolved in water (50 ml) was added to the above-obtained solution over a period of 2 minutes. The thus prepared emulsion was pH-adjusted to precipitate, and the excess salt was filtered out. The emulsion was adjusted to a pH of 6.0, thereby providing a silver benzotriazole emulsion (yield: 200 g).

Preparation of Gelatin Dispersion of Dye Releasing Material (16)

Ten grams of a dye releasing material (16) of the following formula:

and 0.5 g of a surfactant i.e., succinic acid-2-ethylhexyl ester sodium sulfate, and 4 g of tricresyl phosphate (TCP)

were dissolved in 20 ml of cyclohexanone under 6460996 about 60°C, thereby producing a uniform solution. This solution was mixed with a 10 wt% solution of lime-treated gelatin (100 g) under agitation, and the mixture was dispered with homogenizer for 10 minutes at 10,000 rpm.

A coating composition for light-sensitive material was prepared from the following formulation.

(b) Dispersion of dye releasing material 3.5 g

(c) Base precursor (1) of the present inveniton 0.28g

(d) Gelatin (10 wt% aq. sol.) 5 g

(e) Solution having 2,6-dichllro-4-aminophenol (200 ml) dissolved in methanol
 (4 ml)

5

10

15

20

25

The above components of (a) - (e) were mixed and dissolved under heating. The resulting solution was applied to a polyethylene terephthalate film base (180 $\mu\,m$ thick) to form a light-sensitive layer having a wet thickness of 30 $\mu\,m$. The resulting web was dried and imagewise exposed using a tungsten lamp (2000 lux) for 10 seconds and subsequently heated uniformly on a heat block (150°C) for 20 seconds.

The heated sample of light-sensitive material was superimposed on an image-receiving material prepared in Example 2, and subsequently processed as in Example 2 to provide a negative magenta image on the image-receiving material. Measurement with a reflection densitometer showed that the negative image had Dmax 2.06 and Dmin 0.20.

Thus it was found that the compound of 160996 present invention provides excellent effects.

Example 6

Preparation of Gelatin Dispersion of Dye Releasing Material (18)

5

Five grams of each of reducible dye releasing materials of

four grams of the electron donor having the following formula:

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CC-COCHCONH} \\ \text{CH}_{3} \\ \text{COOCH}_{3} \\ \text{CONH (CH}_{2})_{3} \text{O} \end{array}$$

and 0.5 g of succinic acid-2-ethylhexyl ester somether every and 10 g of tricresyl phosphate (TCP) were dissolved in 20 ml of cyclohexanone under heating at about 60°C. This solution was mixed with a 10 wt% solution of gelatin

(100 g) under agitation, and the mixture was dispersed with homogenizer for 10 minutes at 10,000 rpm.

A coating composition for light-sensitive material was prepared from the following formulation.

(a) Silver benzotriazole emulsion containing light-sensitive silver bromide (obtained in Example 5)

5

10

20

(b) Dispersion of dye releasing material 3.5 g
 (obtained in this Example)

10

- (c) Base precursor (1) of the present invention 0.4 g
- 15 (d) 5% Aqueous solution of the following compound: 1.5 ml

$$c_9H_{19} \longrightarrow c_{CH_2CH_2O}H$$

To the above components of (a) - (d) were added 4 ml of water, mixed and dissolved under heating. The resulting solution was applied to a polyethylene terephthalate film base to form a light-sensitive layer having a wet thickness of 30 μ m. The resulting web was dried and imagewise exposed using a tungsten lamp (2000 lux) for 10 seconds and subsequently heated uniformly on a heat block (140°C) for 40 seconds.

The heated sample of light-sensitive material was superimposed on an image-receiving material prepared in Example 2 previously impregnated with water, and subsequently processed as in Example 2 to provide a positive magenta image on the image-receiving material. Measurement with a reflection densitometer using green light showed that the image had Dmax 1.92 and Dmin 0.26.

Thus it was found that the base precursor of the present invention provides excellent effects.

and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A heat developable light-sensitive material comprising a support and formed thereon a heat developable light-sensitive layer, wherein said light-sensitive material contains at least one compound selected from the group consisting of compounds represented by formula (I) or (II) as a base precursor:

$$R-SO_2$$
 $SO_2CH_2COOH \cdot B_{1/m}$ (I)

$$R-SO_2 \xrightarrow{SO_2CH_2COOM_1/m} (II)$$

wherein R represents a substituted or unsubstituted alkyl

group, a substituted or unsubstituted cycloalkyl group,

a substituted or unsubstituted alkenyl group, a sub
stituted or unsubstituted alkynyl group, a substituted

or unsubstituted aralkyl group, a substituted or un-substitued

aryl group or a heterocyclic group; X represents a substituent;

p represents an integer of 0 to 4; B represents a mono
acidic base or diacidic base; M represents an alkali

metal or an alkaline earth metal; and m representsl when

B represents monoacidic base and represents 2 when B

represents diacidic base, and m' represents the valence

number of M.

2. A heat developable light-sensitive material as in claim 1, wherein the heterocyclic ring represented by R is a 5- or 6-membered heterocyclic ring containing at least one of nitrogen atom, an oxygen atom, and a sulfur atom.

5

- 3. A heat developable light-sensitive material as in claim 2, wherein said heterocyclic ring is selected from the group consisting of a pyridyl group, pyrazolyl group, and imidazolyl group.
- 4. A heat developable light-sensitive material as in claim 1, wherein the substituent of said substituted groups represented by R is selected from the group consisting of an alkyl group, an alkyl- or arylsulfonyl group, a sulfamoyl group, an N-alkyl- or N-arylsulfamoyl group, a carbamoyl group, an N-alkyl- or N-arylcarbamoyl group, an alkyl or arylsulfonamido group, an alkyl- or arylacyl amido group, a halogen atom, and a hydroxy-carbonyl group.
 - 5. A heat developable light-sensitive material as in claim 1, wherein B is an organic acid base having a pKa of not less than 7 and having not more than 12 carbon atoms.
 - 6. A heat developable light-sensitive matrial as in claim 5, wherein B has a boiling point of not less

than 150°C.

- 7. A heat developable light-sensitive material as in claim 6, wherein B is a monoacidic or diacidic nitrogen containing sulfur free base.
- 8. A heat developable light-sensitive material as in claim 5, wherein B represents an organic base selected from the group consisting of an aromatic or aliphatic amine, an aromatic or aliphatic diamine, a piperidine, piperadine, a guanidine, a cyclic guanidine, an amidine, a cyclic amidine, a tetraalkylammonium hydroxide.
 - 9. A heat developable light-sensitive material as in claim 1, wherein M represents an atom selected from the group consisting of Na, K, Cs and Ba.
- 10. A heat developable light-sensitive material as in claim 1, wherein X represents a group or atom selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an alkyl group, an aryl group, an alkyl or aryl acylamino group, an alkyl or aryl acyl group, a cyano group, an alkylsulfonylamino group, a nitro group, an arylsulfonylamino group, an alkylsulfonyl group, an arylsulfonyl group, a substituted sulfamoyl group, a carbamoyl group, a substituted carbamoyl group, an alkylthio group, an arylthio group, an alkoxy-

carbonyl group, an aryloxycarbonyl group, an alkyl or arylacyloxy group, and substituted groups thereof at the alkyl or aryl moiety thereof, $-OM_{1/m}$, $-COOM_{1/m}$, $-OH \cdot B_{1/m}$

- (wherein -OH is phenolic), -COOH·B $_{1/m}$, wherein M, B, m and m' have same definitions as defined in claim 1.
- 11. A heat developable light-sensitive material as in claim 1, wherein said base precursor is incorporated in an amount of from 0.001 to 50% by weight based on the total weight of the dry coated layer of the light-sensitive material.
 - 12. A heat developable light-sensitive material as in claim 1, wherein said heat developable light-sensitive layer comprises of a silver halide emulsion layer.
 - 13. A heat developable light-sensitive material as in claim 12, wherein said silver halide emulsion contains a sensitizing dye.
 - 14. A heat developable light-sensitive material as in claim 13, wherein the amount of the sensitizing dye is from 0.001 to 20 g per 100 g of silver of the silver halide emulsion.
 - 15. A heat developable light-sensitive material as in clam 12, wherein the light-sensitive material contains a dye providing material which releases or produces a mobile

dye corresponding to or reversely corresponding to a reduction reaction of a silver halide through a reducing agent as a image forming material.

A heat developable light-sensitive material as 15. in claim 12, wherein the light-sensitive material contains at least one image forming material selected from the group consisting of a coupler, a dye which is able to 5 form positive color images by a photographic silver dye bleaching process, a dye having introduced therein a nitrogen-containing heterocyclic ring group, a dyeproviding material which releases a mobile dye by a coupling reaction with a reducing agent which is oxidized by 10 an oxidation reduction reaction with a silver halide or an organic silver salt upon heat development, a nondiffusible image-forming compound which causes self ring closure in the presence of a base to release a diffusible dye, but does not release the dye when the compound reacts 15 with the oxidation product of a developing agent, and a non-diffusible image-forming compound which does not release a dye by itself but releases a dye when the compound reacts with a reducing agent, and a linked donor acceptor compound which is a nondiffusible image-forming compound 20 and causes a donor-acceptor reaction in the presense of a base to release a diffusible dye, but does not substantially release the dye when the compound reacts with the oxidation product of a developing agent.

- 17. A heat developable light-sensitive material as in claim 12, wherein the light-sensitive material contains at least one image forming material selected from the group consisting of a coupler, a dye which is able to
- 5 form positive color images by a photographic silver dye bleaching process, a dye having introduced therein a nitrogen-containing heterocyclic ring group, a dye-providing material which releases a mobile dye by a coupling reaction with a reducing agent which is oxidized by
- an oxidation reduction reaction with a silver halide or an organic silver salt upon heat development, a dyeproviding material which releases a mobile dve as a result of an oxidation-reduction reaction with silver halide or an organic silver salt upon heat development, a non-
- 15 diffusible image-forming compound which causes self ring closure in the presence of a base to release a diffusible dye, but does not release the dye when the compound reacts with the oxidation product of a developing agent, a non-diffusible image-forming compound which does not
- release a dye by itself but releases a dye when the compound reacts with a reducing agent, and a linked donor acceptor compound which is a nondiffusible image-forming compound and causes a donor-acceptor reaction in the presense of a base to release a diffusible dye, but does not substantially
- 25 release the dye when the compound reacts with the oxidation product of a developing agent.

- 18. A heat developable light-sensitive material as in claim 12 wherein the light-sensitive material further comprises at least one of an interlayer, a filter layer, an antihalation layer, a protective layer, and an image 5 fixing layer provided on the support.
 - 19. A heat developable light-sensitive material as in claim 12, wherein said base precursor is incorporated in the silver halide emulsion layer.
- 20. A heat developable light-sensitive material as in claim 12, wherein the light-sensitive material further comprises of an image fixing layer provided on a support other than that for the light-sensitive layer, and said base precursor is incorporated in the image fixing layer.
 - 21. A heat developable light-sensitive material as in claim 10, wherein X represents a group other than a carboxymethylsulfonyl group.
- 22. A method for producing an image, which comprises heat developing a heat developable light-sensitive material comprising a support and formed thereon a heat developable light-sensitive layer, said light-sensitive material contains at least one compound selected from the group consisting of compounds represented by formula (I) or (II) as a base precursor:

$$R-SO_2 \xrightarrow{SO_2CH_2COOH \cdot B_1/m} x_p$$
 (I)

$$R-SO_2 \xrightarrow{SO_2CH_2COOM_{1/m}} Xp$$
 (II)

- 10 wherein R represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted
- aryl group or a heterocyclic group; X represents a substituent; P represents an integer of 0 to 4; B represents a monoacidic base or diacidic base; "represents an alkali metal or an alkaline earth metal; and m represents 1 when B represents monoacidic base and represents 2 when B represents diacidic base, and m' represents the valence number
 - of M.